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Catalysis Today 90 (2004) 151–158

www.elsevier.com/locate/cattod

Methane conversion at low temperature: the combined application of catalysis and non-equilibrium plasma

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Abstract

The combined oxygen-steam reforming of methane was investigated in a non-thermal plasma or dielectric-barrier discharge (DBD). It was found that only CH_4 and O_2 were converted in the plasma, whereas no net conversion of water was detected. A comparison was made between the DBD reactor with an empty discharge gap and with the discharge gap filled by a dielectric material. In the latter arrangement a Ni catalyst on α-alumina was compared with the pure catalyst support. Experimental data are also compared with thermodynamic equilibrium calculations. Plasma activation leads to CO as a main product, which then however oxidises to CO_2 when the catalyst becomes active (>300 °C). The addition of steam to the reactants results in the enhanced formation of hydrogen under conditions where oxygen is completely converted.

Keywords: Syngas; Plasma catalysis; Nickel catalyst; Plasma induced reforming

1. Introduction

Currently, the only economically available route for converting methane, the main component of natural gas, into more valuable products is via synthesis gas [1–6]. Depending on the industrial application and the required CO:H_2 ratio, the process is realised currently by the well-established highly endothermic steam reforming ($CH_4 + 2H_2O \rightarrow 3H_2 + CO$, $\Delta H^\circ = 206\,kJ/mol$), giving a H_2:CO ratio of 3:1 [1]. As an alternative route, especially to obtain the H_2:CO ratio of about 2, as it is required for methanol or Fischer–Tropsch synthesis, the partial oxidation of methane ($CH_4 + (1/2)O_2 \rightarrow 2H_2 + CO$, $\Delta H^\circ = -36\,kJ/mol$), has been intensively investigated during the past 20 years [2]. Both processes are realised in the largest possible scale to make them commercially viable. However, often natural gas resources occur as remote reservoirs or as casing head gas in remote locations. Due to the high transport or storage costs of gas, costs for catalytically operating systems are pushed beyond commercial interest.

Meanwhile, an increasing number of applications and manufacturing processes that require syngas or hydrogen in much smaller quantities than refineries, ammonia or methanol plants emerge, e.g. in fuel cell applications [6]. Another important field which is recently emerging, is the development of new environmentally friendly technologies, such as the control of CO_2 emission or the utilisation of biogas (CH_4 and CO_2). In these fields, significant advantages are currently expected from non-traditional approaches to catalysis.

One of these new approaches is to combine heterogeneous catalysis with the chemical activation of reactants by an electric gas discharge or plasma. Most promising are the non-thermal e.g. microwave [7], corona [8], dielectric-barrier discharges [9] and others [10]. In a non-equilibrium plasma gaseous species are chemically excited or dissociated directly by electron impact, while the temperature of the reactants, the gas temperature, remains relatively low and thus product distributions far from chemical equilibrium may be obtained. Plasma processes offer a unique way to induce gas phase reactions by electron collisions, but they are often less selective than catalytic processes. Catalytic reactions on the other hand can give high selectivity, but require a certain gas composition, an active catalyst, high temperature or its strict control. Therefore, such a combination of plasma activated reactions with a selective catalytic process seems to be a challenge and a promising way to enhance traditional catalytic processes.

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0920-5861/$ – see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.cattod.2004.04.021

Non-equilibrium plasma obtained in a dielectric-barrier discharge (DBD) has been used for several chemical and catalytic processes as reviewed recently by Kogelschatz [11]. Examples are the decomposition of nitrogen and sulphur oxides in flue gases [12], abatement of volatile organic compounds [13,14], or treatment of diesel exhaust gases [15]. This type of discharge has been also used for methane reforming processes: dry reforming to syngas [16,17], reforming of higher hydrocarbons or oxygenates [18–20], steam reforming [15,21,22] and partial oxidation [23,24]. Since the DBD allows the direct insertion of a dielectric material into the discharge gap, it has attracted considerable interest for combining the plasma-chemical activation of reactants with heterogeneous catalysis under atmospheric pressure and relatively low temperatures.

In this paper, we present the application of non-equilibrium plasma for the combined oxygen-steam reforming of methane in a DBD reactor at relatively low temperatures. To separate the effect of the plasma activation from surface and catalytic processes, the reaction is also investigated in an empty DBD reactor as well as over pure catalyst support. Finally, the amount of water addition and catalyst amount in the discharge gap is studied.

2. Experimental

2.1. DBD reactor

The DBD reactor, as described [23–25], consists of two coaxial quartz tubes with a wall thickness of 1.5 mm. The discharge gap between the tubes is 1.5 mm and the length of the discharge zone is 10 cm, resulting in the reaction volume of approximately 7 cm^3. As high voltage electrode, a metal layer inside the inner tube was used and the outer electrode was made from a metal spiral, also serving as electrical heater. To drive the discharge an AC high voltage was generated with a maximum of 10 kV_{eff} at 25–40 kHz. The discharge power was calculated from the time-averaged product of discharge voltage and current. The accuracy is about 10%. The temperature was measured at the outside tube of the reactor, since a thermocouple inside the catalyst bed interferes with the discharge.

2.2. Catalytic measurements

The catalytic tests were conducted under atmospheric pressure in the temperature controlled DBD reactor in the temperature range from 100 to 400 °C. Total gas flow rates (air, CH_4 and Ar) were from 85 to 340 sccm. The composition of the feed gas was varied, changing the molar ratio of CH_4:O_2 from 1:1 to 4:1. The gas mixture was passing through a temperature controlled bubbler to saturate it with steam to concentrations from 5.6 to 19.9%. About 10% of Ar was added to allow monitoring the total volume flow rate at the reactor outlet and the volume variations during the reaction. The addition of Ar has some effect on the plasma power at a given applied voltage, however, variation of the Ar flow showed that the influence on conversion and product distribution at a given plasma power is not significant.

The amount of catalytic material in the discharge zone was varied from 0 to 6 g. The discharge gap was left empty for experiments with only plasma activation. For tests with catalyst and plasma, 2 g of sample were used filling about 1/3 of the discharge volume and 6 g, filling the entire discharge gap. α-Al_2O_3 and a commercial Ni catalyst (Süd-Chemie G90B), with a specific surface area 9 and 6 $m^2\,g^{-1}$, respectively, grains sizes 0.71–1.00 mm, were used. The Ni catalyst was first calcinated in air at 700 °C for 4 h. For the catalytic measurements, unreduced (NiO/α-Al_2O_3) and reduced samples were tested (reduction in 6.7% H_2 in Ar, 150 sccm, 200–450 °C, 5 K min^{-1} and at 450 °C for 1 h). The CH_4 and O_2 conversions are defined as the percentage of the CH_4 and O_2 that have reacted. The calculation of product selectivity was based on the carbon in the methane converted for CO and CO_2, and on the hydrogen from converted CH_4 for H_2O and H_2.

Non-dispersive infrared spectrometry (NDIR) and mass spectrometry (MS) were used to measure H_2O, CH_4, O_2 and CO_2. CO was analysed only by NDIR and H_2 by MS. A GC/FID (gas chromatograph equipped with a flame ionisation detector) was used to analyse the hydrocarbons formed. For calibration, test gas mixtures with known concentrations were used. Measurement and calibration errors are within 5%, however calculated selectivities may have a larger error at low conversion. The specific energy input (SEI in kJ/mol) is defined as the electric power supplied to the plasma divided by the gas flow.

3. Results

3.1. Combined oxygen-steam reforming of methane in a DBD reactor with an empty gap

As shown in Table 1, plasma induces methane conversion in the combined oxygen-steam reforming of methane. As it was already reported [25,26], when the steam was added to the reagent mixture, in the presence of plasma, a net consumption of water was not observed. The only converted reagents were methane and oxygen, whereas the water output was always higher than input values. Because of this, the hydrogen selectivity was calculated under the assumption that only CH_4 but not H_2O contributes to H_2-formation. CO, CO_2, H_2O and H_2 are the main products of plasma activated methane reforming. Traces of C_2–C_4 hydrocarbons (less than 0.5%) were also detected and carbon and waxes deposition on the reactor wall was found after the measurements.

Both conversions of CH_4 and O_2 increase with the input plasma power and temperature and they decrease with increasing the total flow rate (decreasing SEI). The plasma

Table 1
The influence of temperature, reagent flow rate, specific energy input and the CH_4:O_2 ratio on the methane and oxygen conversions and the ratio of H_2/H_2O and CO/CO_2 (7.4% steam, empty DBD reactor, i.e. without dielectric filling)

Temperature (°C)	Total flow rate (sccm)	Input energy (W)	SEI (kJ/mol)	CH_4 conversion (%)			O_2 conversion (%)			H_2/H_2O ratio			CO/CO_2 ratio		
				1:1	2.5:1	4:1	1:1	2.5:1	4:1	1:1	2.5:1	4:1	1:1	2.5:1	4:1
200	85	27	376	54	29	18	84	94	92	0.06	0.23	0.42	1.2	3.2	4.0
200	170	27	200	30	17	12	46	61	58	0.09	0.16	0.2	3.0	4.5	5.0
200	340	28	107	15	9	10	25	30	32	0.14	0.21	0.25	4.7	5.6	5.5
300	85	31	432	75	40	25	96	96	95	0.15	0.4	0.64	1.2	4.0	5.2
300	170	32	237	55	28	18	80	85	88	0.05	0.18	0.26	2.4	5.0	5.7
300	340	32	122	28	15	12	40	46	50	0.07	0.17	0.22	5.0	7.6	7.0
400	85	34	474	76	40	35	97	96	96	0.17	0.4	0.6	1.7	2.7	6.7
400	170	33	244	61	28	30	90	85	95	0.08	0.18	0.37	5.5	8.2	7.6
400	340	32	122	35	16	20	52	46	60	0.08	0.17	0.26	6.0	5.5	8.7

1:1, 2.5:1, 4:1 denote the CH_4:O_2 ratios.

power was applied at a constant voltage and due to the lower gas density at higher temperature, this leads to the increase from 27 to 32 W between 200 and 400 °C. This is in part also the reason for the increasing conversions at higher temperature. On the other hand, in addition to the methane activation by electron impact, also thermally activated reactions, such as hydrogen abstraction by atomic hydrogen, are involved in the process leading to an increase in conversion with temperature.

Considering the product distribution, CO and H_2O are the main products; however, the H_2/H_2O and CO/CO_2 ratios depend on the total flow and input gas composition. When increasing the total flow at constant power input (decreasing specific energy input SEI), the H_2/H_2O ratio is decreasing. At the same time, an increase of the CO/CO_2 ratio is observed. At a lower oxygen concentration in the mixture higher CO/CO_2 is obtained, however with decreasing CH_4 conversion and H_2/H_2O ratio.

3.2. The effect of dielectric material in the discharge zone on the methane reforming

Figs. 1–6 show the effect of a dielectric material in the discharge zone on the conversions of methane (Fig. 1) and oxygen (Fig. 2) and on the selectivity to H_2, H_2O, CO and CO_2 (Figs. 3–6, respectively). The data presented were measured at 300 and 400 °C at a total gas flow rate of 170 sccm, 7.4% H_2O, CH_4:O_2 = 2.5:1, a plasma power of about 30 W (SEI = 223 kJ/mol) and 2 g of sample in the discharge gap. Below 300 °C the reactant conversion and product selectivities did not depend significantly on the material in the discharge and were about the same as obtained in the empty DBD reactor (Table 1). Equilibrium data are also presented, calculated using the STANIAN program [27]. In these calculations, the oxidation of methane is considered as the main reaction and the water gas shift reaction ($CO + H_2O \rightarrow H_2 + CO_2$) as the secondary reaction.

It must be noticed, that no conversion of CH_4 and O_2 was detected over the investigated materials in the absence

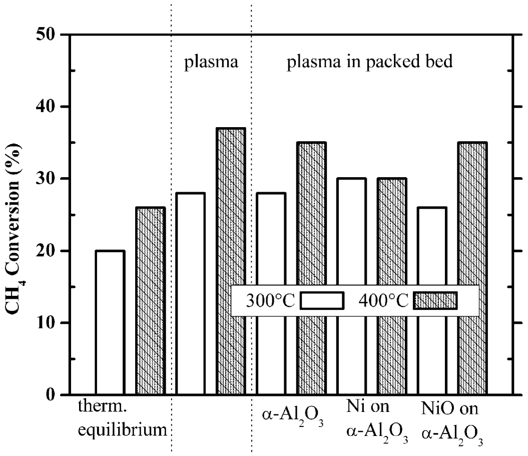

Fig. 1. The methane conversion at equilibrium and in a DBD reactor without or with catalytic material in the discharge gap (at 300 and 400 °C, total gas flow rate 170 sccm, CH_4:O_2 = 2.5:1, H_2O 7.4%, 30 W, SEI = 223 kJ/mol, 2 g of sample, grains size 0.7–1.0 mm).

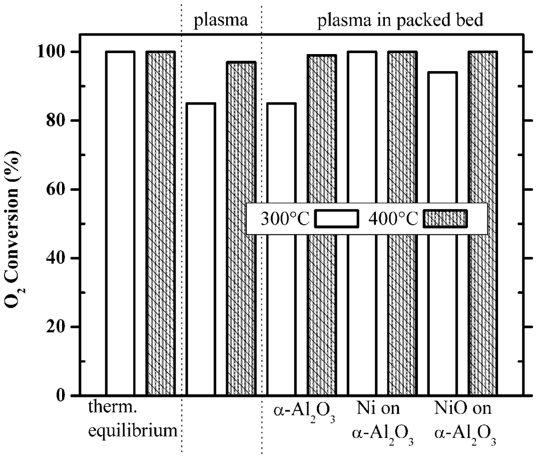

Fig. 2. The oxygen conversion at equilibrium and in a DBD reactor without or with catalytic material in the discharge gap, conditions as in Fig. 1.

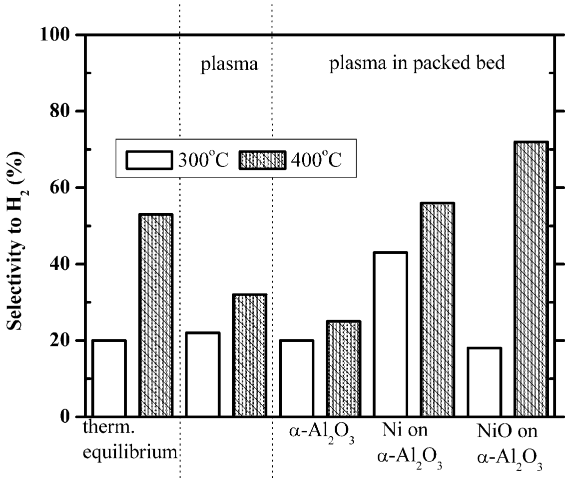

Fig. 3. The selectivity to H_2 at equilibrium and in a DBD reactor without or with catalytic material in the discharge gap, conditions as in Fig. 1.

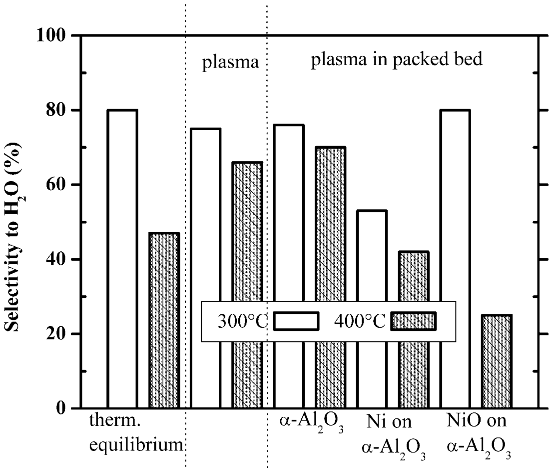

Fig. 4. The selectivity to H_2O at equilibrium and in a DBD reactor without or with catalytic material in the discharge gap, conditions as in Fig. 1.

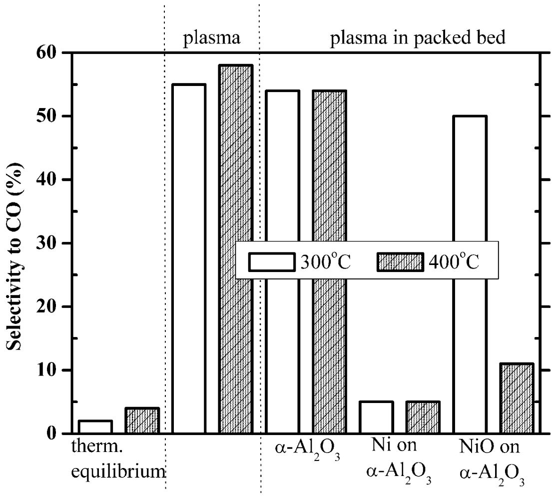

Fig. 5. The selectivity to CO at equilibrium and in a DBD reactor without or with catalytic material in the discharge gap, conditions as in Fig. 1.

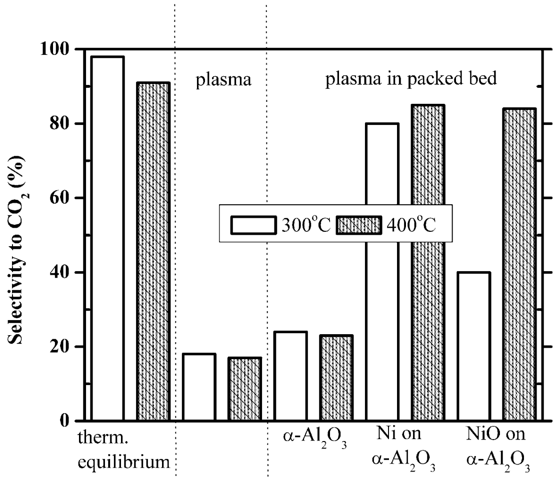

Fig. 6. The selectivity to CO_2 at equilibrium and in a DBD reactor without or with catalytic material in the discharge gap, conditions as in Fig. 1.

of the discharge below 400 °C. As it was observed in an empty DBD reactor, CO, CO_2, H_2O and H_2 were the main products and traces of C_2–C_3 hydrocarbons and methanol were also detected. In the presence of the discharge, the methane conversion exceeds the equilibrium values at these temperatures. The dependence of the CH_4 conversion on the material in the discharge gap is rather small, ranging from about 30 to 40%.

Oxygen conversion is 100% at chemical equilibrium, and as it is shown in Fig. 2, total oxygen conversion is only obtained over the nickel catalyst and over NiO at 400 °C. The 100% conversion of oxygen over the nickel catalyst at both temperatures indicates catalytic activity. The oxygen conversion never exceeded 96%, when the discharge was operating in the empty gap and over α-Al_2O_3. Comparing the product selectivity calculated for thermodynamic equilibrium with the results obtained in the discharge, we can see significant differences, especially for CO and CO_2. At such low temperatures, CH_4 is mainly converted to CO_2, H_2O and H_2 at thermodynamic equilibrium, whereas plasma produces mainly CO and H_2O. At low temperatures, CO is not formed under equilibrium conditions, the selectivity is only 4% at 400 °C. In the discharge, CO formation greatly exceeds the equilibrium value, showing the non-equilibrium character of plasma activation or electron impact dissociation. The highest CO selectivity was obtained in the empty DBD whereas the presence of material surface apparently promotes the surface oxidation of CO to CO_2, with the rate increasing in the following order: α-Al_2O_3 < NiO/α-Al_2O_3 < Ni/α-Al_2O_3. The equilibrium value is obtained at 400 °C only over the Ni catalyst.

Considering the selectivity to H_2 and H_2O in Figs. 3 and 4, it is seen that the equilibrium composition is approached only over NiO and that the highest selectivity to H_2 is obtained at 400 °C. In the reactor with empty gap and in the presence of α-Al_2O_3 the H_2 selectivity is lower. Without an active catalyst, the H_2 selectivity did not exceed 20%, whereas Ni catalyst promotes hydrogen production.

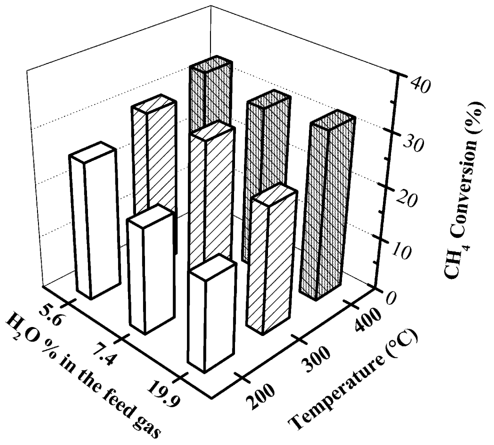

Fig. 7. The methane conversion vs. temperature and the steam addition in a DBD reactor over Ni/α-Al_2O_3 catalyst (total gas flow rate 170 sccm, $CH_4:O_2 = 5/2:1$, 29 W, 2 g of the catalyst, grains size 0.7–1.0 mm).

The selectivity to water is changing in the opposite way as the selectivity to hydrogen (Fig. 4).

3.3. Plasma catalytic reforming: the effect of steam and catalyst amount

In Figs. 7 and 8 the influence of steam concentration in the feed gas on the methane and oxygen conversions is shown. The influence of the steam on the reagents conversions is most noticed at 200 °C, where both conversions are decreasing with increasing steam concentration. At 300 °C and above the changes of the conversions differ only slightly, the oxygen conversion is 100% and, as observed before in Figs. 1 and 2, the methane conversion saturates around 30%.

In Figs. 9 and 10 the H_2/H_2O and CO/CO_2 ratios are plotted for these experiments. At low temperature (200 °C), CO is the main product and not strongly dependent on the steam addition. At 300 °C, the products of total methane oxidation (CO_2 and H_2O) dominate and at 400 °C hydrogen becomes a dominant product. At 400 °C, the CO selectivity is always less than 4%. Significant variations of CO/CO_2 and H_2/H_2O ratios are observed with 7.4% steam addition at the temperature range investigated. To explain this, we assume that the Ni catalyst promotes the water gas shift reaction (Section 3.2), however only if oxygen is completely converted as shown in Fig. 8 at 300 and 400 °C. So as observed, the hydrogen formation follows the assumption and it is increasing with the increasing steam addition and temperature. Obviously, the addition of steam promotes hydrogen formation, however, if oxygen conversion is not complete, some hydrogen is lost to oxidation.

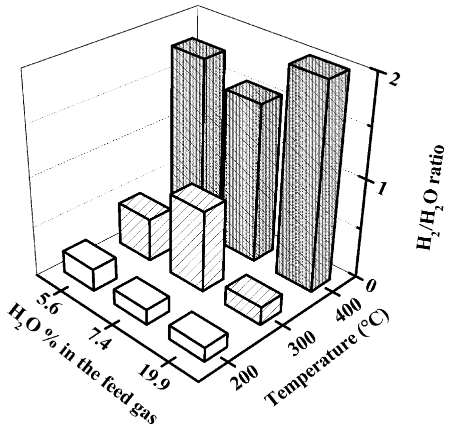

Fig. 9. The H_2/H_2O ratio vs. temperature and the steam addition in a DBD reactor over Ni/α-Al_2O_3 catalyst, conditions as in Fig. 7.

As shown in Figs. 11 and 12, the amount of nickel catalyst in the discharge gap influences both the reagent conversions and the product distribution. Keeping the SEI constant at 181 kJ/mol, higher methane and oxygen conversions were observed in the DBD reactor filled only partially (1/3 of the discharge volume) with the catalyst. Looking at the ratio of CO/CO_2 and H_2/H_2O, one can see that in the partially filled DBD reactor CO production at low temperature (200 °C) and hydrogen formation at higher temperature (400 °C) are detected. When filling the discharge gap with a catalyst, the discharge is operating only between the grains and its vol-

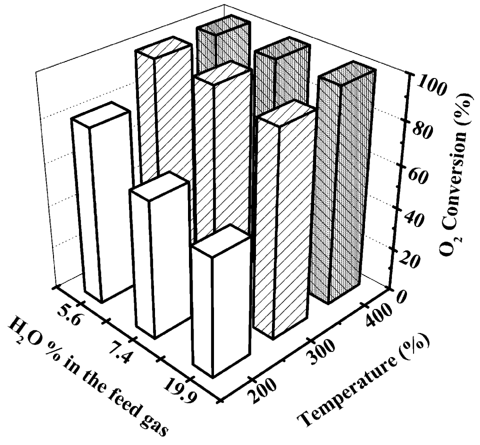

Fig. 8. The oxygen conversion vs. temperature and the steam addition in a DBD reactor over Ni/α-Al_2O_3 catalyst, conditions as in Fig. 7.

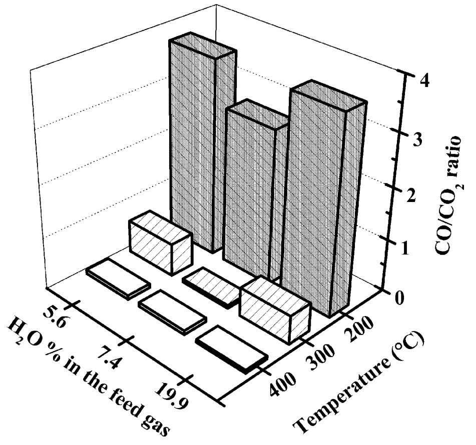

Fig. 10. The CO/CO_2 ratio vs. temperature and the steam addition in a DBD reactor over a Ni/α-Al_2O_3 catalyst, conditions as in Fig. 7.

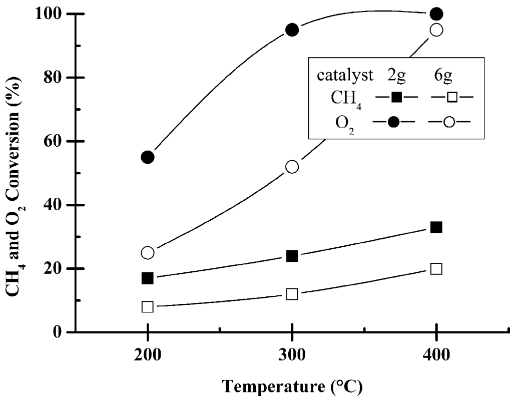

Fig. 11. The methane and oxygen conversions vs. temperature over a different catalyst amount in the discharge zone on (total gas flow rate 170 sccm, CH_4:O_2 = 5/2:1, H_2O 19.9%, 27 W, SEI = 181 kJ/mol, sample grains size 0.7–1.0 mm).

ume is reduced. Since at the low temperatures investigated, the methane activation requires electron impact dissociation by the plasma and no reaction was observed over the catalytic material without operating discharge, the decreasing discharge volume results in decreasing conversion, as observed in Fig. 11. It should be mentioned here, that inserting a catalytic material into the plasma affects its properties, as already described by Kraus et al. [16]. The presence of the grains is likely to lead to some surface reactions and loss of active species and probably to a reduction of their concentration in the gas phase.

When the discharge gap was completely filled by the catalyst, the plasma causes ignition in the reactor and the autothermal reaction can proceed without operating the discharge. In that case, significant overheating while operating the discharge occurred and it was more difficult to maintain stable plasma conditions. After several hours on stream the catalyst bed developed three different zones, including some coke deposition close to the outlet. During oxygen reforming of methane without steam addition [23,24] the dependence on gas flow and plasma power shows that the plasma induced reactions are kinetically limited in the current reactor, whereas the residence time in the catalyst bed is sufficient even for a partially filled gap. The lower selectivity to CO and H_2 is probably the result of their oxidation on the catalyst surface.

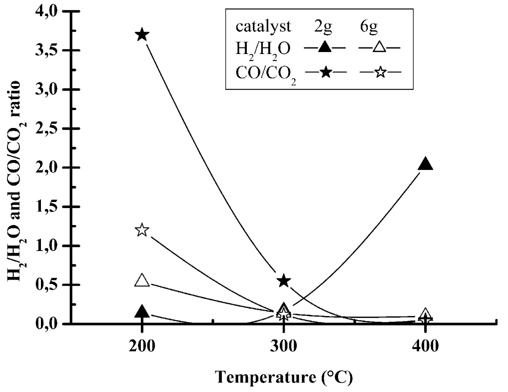

Fig. 12. The H_2/H_2O and CO/CO_2 ratios vs. temperature and over a different catalyst amount in the discharge zone, conditions as in Fig. 11.

4. Discussion

4.1. Plasma reforming of methane

A plasma process employing a DBD was applied for the combined oxygen-steam reforming of methane at temperatures below 400 °C under atmospheric pressure. In the reactor with an empty discharge gap conditions are obtained, under which gas phase reactions induced by the discharge dominate the reagent conversion and product selectivities. In a DBD most of the discharge energy is used to produce and accelerates electrons, which then generate highly active species (metastables, radicals and ions). Methane and oxygen is chemically activated directly by electron collisions. Although the average electron energy in a DBD is below 10 eV [11], oxygen is effectively dissociated by electron impact ($e + O_2 \rightarrow e + O + O$). Active oxygen radicals react then with methane by hydrogen abstraction producing OH radicals [15]. These are also an extremely efficient oxidant (oxidising potential 2.8 eV) and can react further with methane to form water. The electron impact dissociation of methane requires about 9–12 eV, as compared to 6–8 eV for oxygen. Considering the high bond energy of 11.2 eV for CO, it is rather stable in the plasma. Therefore, CO seems to be produced as the primary product of plasma assisted methane-oxygen reforming. It is also likely that some CO_2 formed is subsequently dissociated in the discharge to CO and active oxygen atoms. Concerning the efficiency of electron impact dissociation of CO_2 in a DBD, as reported by Kogelschatz [11], about 40% of the electron energy can be utilised for the CO_2 dissociation. However, as it has also been reported by Zheng et al. [28], the presence of oxygen suppresses the CO_2 conversion to CO, also indicating that CO is the primary product.

In the current experiments, the only reagents converted are CH_4 and O_2 whereas the concentration of steam was always higher at the output than at the input. It is difficult to assess the role of steam in plasma assisted methane-oxygen reforming. As recently published by Hammer et al. [15], the H_2O conversion in a DBD reactor was negligible, indicating insufficient steam activation by plasma; less than 5% of the input energy was available for water dissociation. However, about 69% of the OH radicals generated from water dissociation were reported to be consumed by the hydrogen abstraction from the CH_4, resulting in CH_3 radicals and water.

4.2. Plasma catalytic reforming of methane

Catalytic material in the discharge zone of plasma catalytic processes is used to improve the selectivity and efficiency of plasma processes by surface reactions. Our motivation for putting a nickel catalyst, well known as a good catalyst for methane steam reforming, in the discharge zone was to improve the plasma activation together with the catalyst and also to try controlling or changing the product distribution. As we showed in the present study, the presence of α-Al_2O_3 in the discharge zone does not influence significantly the reagent conversions as compared to the empty DBD reactor. Also the product distribution is not changing significantly, only a small increase of CO_2 formation can be attributed to the surface oxidation of CO to CO_2. When Ni catalyst is present in the metallic or the oxidised (NiO) form, the conversions are not changed significantly in comparison to the empty DBD, but the products selectivities are changed. It is necessary to point out that the changes in selectivities are noticed only if the temperature is high enough for the catalytic material to become itself active, i.e. when the metallic Ni surface starts to be partially oxidised at 300 °C and the NiO surface, on the other hand, partially reduced, as was observed at 400 °C. Results on temperature programmed reduction and oxidation are given in [23]. The presence of the Ni catalyst results in total oxygen conversion, which was not obtained in an empty DBD or over α-Al_2O_3. Only if oxygen is fully converted hydrogen is a major reaction product. NiO, when reduced at 400 °C shows the same behaviour; its re-oxidation forces the surface oxidation of CO to CO_2. The partially reduced NiO surface in combination with plasma was found most attractive for hydrogen formation, with a selectivity of about 70%.

Although the influence of steam addition to the reaction in a DBD is not well understood, in the reaction over the Ni catalyst it is much more evident. Its addition increases the hydrogen formation, indicating the WGSR. We could also expect that the presence of steam in the reagent mixture, due to the adsorption on the catalyst surface has a strong influence on the state of catalyst surface during discharge operation. We should also remember that in a DBD there are extended surface discharges (on the dielectric material) covering a much larger area than the original discharge streamers in an empty gap. The catalytic material, especially the surface of the catalyst grains, is also influenced by strong electric filed. The other aspect is that under atmospheric conditions, due to a large numbers of particle collisions, most of the input power is converted to heat transferred to the catalytic material. The discharge causes probably formation of hot spots in the catalytic material [29]. Such hot spots could be responsible for the catalyst activation and the observed selectivity. It can be one explanation of the measured activity of the catalyst in the presence of the discharge. However, the existence of such hot spots is difficult to ascertain. With the addition of steam, no catalytic conversion was observed when the plasma is switched off at such low temperatures (up to 400 °C). In our opinion the discharge accelerates the adsorption–desorption processes, by activating the adsorbed molecules and, probably, by activating also the catalyst surface. In our study, net water conversion is not observed, however, its desorption from the surface can be accelerated by the discharge.

5. Conclusions

A plasma catalytic process employing a DBD reactor was applied for the combined oxygen-steam reforming of methane at the temperature range below 400 °C. When operating the discharge, only methane and oxygen were converted. By the combining of the DBD and a Ni catalyst the conversion of methane was not improved, but full oxygen conversion was achieved. At a sufficient temperature to maintain the Ni catalytically active the product selectivities changed significantly. The effect of the steam led to enhanced hydrogen yield (WGS), provided oxygen was fully converted. The selectivity to H_2 of about 70% over NiO/Al_2O_3 was achieved. Plasma was found to activate the reagents and accelerate the adsorption–desorption processes, whereas the oxidation state of catalyst is responsible for the surface reactions.

Acknowledgements

This research was supported by the E.U. (contract number ICA2-CT-2000-10004).

References

[1] J.R. Rostrup-Nielsen, Catal. Today 63 (2–4) (2000) 159.

[2] A.P.E. York, T. Xiao, M.L.H. Green, Top. Catal. 22 (3–4) (2003) 345.

[3] J.R. Rostrup-Nielsen, Proceedings of the NATO ASI: Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges and Opportunities, 6–19 July 2003, Vilamoura, Algarve, Portugal, p. 199.

[4] D. Trimm, Proceedings of the NATO ASI: Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges and Opportunities, 6–19 July 2003, Vilamoura, Algarve, Portugal, p. 39.

[5] D. Trimm, Proceedings of the NATO ASI: Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges and Opportunities, 6–19 July 2003, Vilamoura, Algarve, Portugal, p. 51.

[6] H. Stitt, Proceedings of the NATO ASI: Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges and Opportunities, 6–19 July 2003, Vilamoura, Algarve, Portugal, p. 123.

[7] V.L. Zholobenkon, E.R. House, Catal. Lett. 89 (1–2) (2003) 35.

[8] Ch. Liu, A. Marafee, R. Mallinson, L. Loban, Appl. Catal. 164 (1997) 21.

[9] K. Shimizu, T. Hirano, T. Oda, IEEE-IAS Conference (1998), pp. 1865–1870.

[10] K. Krawczyk, M. Mlotek, Appl. Catal. B: Environ. 30 (2001) 233.

[11] U. Kogelschatz, Plasma Chem. Plasma Process. 23 (1) (2003) 1.

[12] H. Ma, P. Chen, M. Zhang, X. Lin, R. Ruan, Plasma Chem. Plasma Process. 22 (2) (2002) 239.

[13] F. Holtzer, U. Roland, F.-D. Kopinke, Appl. Catal. B: Environ. 38 (2002) 163.

[14] U. Roland, F. Holtzer, F.-D. Kopinke, Catal. Today 73 (2002) 315.

[15] Th. Hammer, Th. Kappes, M. Baldauf, Plasma Sources Sci. Technol. 11 (2002) A196–A201.

[16] M. Kraus, B. Eliasson, U. Kogelschatz, A. Wokaun, Phys. Chem. Chem. Phys. 3 (2001) 294.

[17] M. Kraus, PhD Thesis, Swiss Federal Institute of Technology, Zurich, 2001.

[18] K. Zhang, B. Eliasson, U. Kogelschatz, Energy Fuels 15 (2001) 395.

[19] K. Zhang, B. Eliasson, U. Kogelschatz, Ind. Eng. Chem. Res. 41 (2002) 1462.

[20] J.J. Zou, Y.P. Zhang, Ch.-J. Liu, Y. Li, B. Eliasson, Plasma Chem. Plasma Process. 23 (1) (2003) 69.

[21] Th. Hammer, Th. Kappes, M. Baldauf, in: A. Haljaste, T. Plank (Eds.), Proceedings of the HAKONE 8, Tatru, Estonia, 2002, p. 196.

[22] Th. Hammer, Th. Kappes, M. Baldauf, Fuel Chem. Div. Preprints 46 (1) (2001).

[23] M. Heintze, B. Pietruszka, Catal. Today 89 (1–2) (2004) 21.

[24] B. Pietruszka, K. Anklam, M. Heintze, Appl. Catal. A. General 261 (2004) 19.

[25] B. Pietruszka, M. Heintze, in: A. Haljaste, T. Plank (Eds.), Proceedings of the HAKONE 8, Tatru, Estonia, 2002, p. 166.

[26] B. Pietruszka, K. Anklam, M. Heintze, Proceedings of the 16th International Symposium on Plasma Chemistry, Taormina, Italy, June 22–27, 2003.

[27] Available through the web: http://www.stokes.lance.colostate.edu.

[28] G. Zheng, J. Jiang, Y. Wu, R. Zhang, H. Hou, Plasma Chem. Plasma Process. 23 (1) (2003) 59.

[29] X. Zhang, D.O. Hayward, M.P. Mingos, Catal. Lett. 88 (1–2) (2003) 33.